

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re:	DeSimone <i>et al.</i>	Confirmation No.:	8879
Appl. No.:	10/583,570	Group Art Unit:	1617
Filed:	March 5, 2007		
For:	METHODS FOR FABRICATING ISOLATED MICRO- AND NANO-STRUCTURES USING SOFT OR IMPRINT LITHOGRAPHY		

MAIL STOP PG-PUB
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

**REQUEST FOR A CORRECTED OR REVISED PATENT APPLICATION
PUBLICATION UNDER 37 C.F.R. §1.221(b)**

Sir:

Certain printing errors appear in the patent application publication identified above. The errors appear in the claims and are apparent from the USPTO records. It is respectfully requested that a corrected patent application publication be granted for the above-identified application, in accordance with 37 C.F.R. §1.221(b). This request is made in order to correct the material mistakes incurred through the fault of the Patent Office.

In reviewing Publication No. US-2009-0028910-A1 published January 29, 2009, for the above-referenced application, Applicants note the following errors:

1) On page 38 of the publication, Claim 60 is incorrect, showing “The method of claim 59, wherein the particle comprises a biodegradable polymer.” This should be corrected to read “The method of claim 57, wherein the particle comprises a biodegradable polymer.” A copy of the Amendment filed on June 16, 2006 is attached, indicating that the Claim 60 was amended to change its dependency to claim 57, instead of claim 59.

Republication is requested to set forth the correction in Claim 60. It is respectfully requested that this error be corrected and that page 38 of the publication be republished.

It is not believed that fees are required, however, any required fees therefore are hereby authorized to be charged to Deposit Account No. 16-0605.

Respectfully submitted,

/w. murray spruill/

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TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A SUBMISSION UNDER 35 U.S.C. 371		ATTORNEY'S DOCKET NUMBER 421/90 PCT/US U.S. APPLICATION NO. (If known, see 37 CFR 1.5)
INTERNATIONAL APPLICATION NO. PCT/US04/42706	INTERNATIONAL FILING DATE 12/20/2004	PRIORITY DATE CLAIMED 12/19/2003
TITLE OF INVENTION METHODS FOR FABRICATING ISOLATED MICRO-AND NANO- STRUCTURES USING SOFT OR IMPRINT LITHOGRAPHY		
APPLICANT(S) FOR DO/EO/US UNIVERSITY OF NORTH CAROLINA, Joseph M. DeSimone, Jason P. Rolland, Ansley E. Exner, Edward T. Samulski, R. Jude Samulski, Benjamin W. Maynor, Larken E. Euliss, Ginger Denison Rothrock		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information: <ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a submission under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a submission under 35 U.S.C. 371. 3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371 (f)). The submission must include items (5), (6), (9) and (21) indicated below. 4. <input checked="" type="checkbox"/> The US has been elected (Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c)(2)) <ol style="list-style-type: none"> a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> has been communicated by the International Bureau. c. <input checked="" type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371 (c)(2)). <ol style="list-style-type: none"> a. <input type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input checked="" type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). <p>Items 11 to 20 below concern document(s) or information included:</p> <ol style="list-style-type: none"> 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 12. <input type="checkbox"/> An assignment document for recording. A separate 13. <input type="checkbox"/> A preliminary amendment. 14. <input type="checkbox"/> An Application Data Sheet under 37 CFR 1.76. 15. <input type="checkbox"/> A substitute specification. 16. <input type="checkbox"/> A power of attorney and/or change of address letter. 17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 37 CFR 1.821 - 1.825. 18. <input type="checkbox"/> A second copy of the published International Application under 35 U.S.C. 154(d)(4). 19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). 		

"Express Mail" mailing number EV 851590904 US
 Date of Deposit June 19, 2004
 I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail to Addressee" service under 37 C.F.R. 1.10 on the date indicated above and is addressed to the Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.
 Stacie H. Boswell

Stacie H. Boswell

This collection of information is required by 37 CFR 1.414 and 1.491-1.492. The information is required to obtain or retain a benefit by the public, which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 15 minutes to complete, including gathering information, preparing, and submitting the completed form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS.
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U.S. APPLICATION NO. (if known, see 37 CFR 1.5)		INTERNATIONAL APPLICATION NO. PCT/US04/42706		ATTORNEY'S DOCKET NUMBER 421/90 PCT/US	
20. Other items or information: Copy of Amendment Pursuant to PCT Article 34 filed May 26, 2005 with Chapter II Demand Copy of Amendment Pursuant to PCT Article 34 filed May 30, 2006					
The following fees have been submitted				CALCULATIONS	PTO USE ONLY
21.	<input checked="" type="checkbox"/>	Basic national fee (37 CFR 1.492(a))	\$300	\$ 300	
22.	<input checked="" type="checkbox"/>	Examination fee (37 CFR 1.492(c)) If the written opinion prepared by ISA/US or the international preliminary examination report prepared by IPEA/US indicates all claims satisfy provisions of the PCT Article 33(1)-(4)	\$0		
		All other situations	\$200	\$ 200	
23.	<input checked="" type="checkbox"/>	Search fee (37 CFR 1.492(b)) If the written opinion of the ISA/US or the international preliminary examination report prepared by IPEA/US indicates all claims satisfy provisions of the PCT Article 33(1)-(4)	\$0		
		Search fee (37 CFR 1.445(a)(2)) has been paid on the international application to the USPTO as an International Searching Authority	\$100		
		International Search Report prepared by an ISA other than the US and provided to the Office or previously communicated to the US by the IB.	\$400		
		All other situations	\$500	\$ 100	
TOTAL OF 21, 22 and 23 =				\$ 600	
<input checked="" type="checkbox"/> Additional fee for specification and drawings filed in paper over 100 sheets (excluding sequence listing IN COMPLIANCE WITH 37 cfr 1.821(c) or (e) or computer program listing in an electronic medium) (37 CFR 1.492(j)). The fee is \$250 for each additional 50 sheets of paper or fraction thereof.					
Total Sheets	Extra sheets	Number of each additional 50 or fraction thereof (round up to a whole number)	RATE		
153	-100 =	53	/50 =	2	x \$250
				\$ 500	
Surcharge of \$130.00 for furnishing any of the search fee, examination fee, or the oath or declaration after the date of the commencement of the national stage (37 CFR 1.492(h)).				\$ 0	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	137 - 20 =	117	X \$50	\$5,850	
Independent claims	5 - 3 =	2	X \$200	\$ 400	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$360	\$ 360	
TOTAL OF ABOVE CALCULATIONS =				\$7,710	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. Fees above are reduced by 1/2.				\$7,710	
SUBTOTAL =				\$7,710	
Processing fee of \$130.00 for furnishing the English translation later than 30 months from the earliest claimed priority date (37 CFR 1.492(i)).				\$ 0	
TOTAL NATIONAL FEE =				\$7,710	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				\$ 0	
TOTAL FEES ENCLOSED =				\$7,710	
				Amount to be refunded:	\$
				Amount to be charged:	\$

DUPLICATE FOR DEPOSIT ACCOUNT

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

- a. ☒ A check in the amount of \$ 7,710.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 50-0426. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the International Application to pending status.

SEND ALL CORRESPONDENCE TO:

Aries A. Taylor, Jr. 12 June 2007
SIGNATURE:

Aries A. Taylor, Jr.
NAME

39,395
REGISTRATION NUMBER

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UNITED STATES OF AMERICA

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I hereby certify that this paper or fee is being deposited with the United
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Stacie H. Boswell

Stacie H. Boswell

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
PCT ELECTED OFFICE (EO/US)

In re Application of: THE UNIVERSITY OF NORTH CAROLINA AT CHAPEL
HILL ET AL.

PCT Application No.: PCT/US04/42706

Filed: 20 December 2004
(Priority Date – 19 December 2003)

Attorney Docket No.: 421/90 PCT

For: METHODS FOR THE FABRICATION ISOLATED MICRO- AND NANO-
STRUCTURES USING SOFT OR IMPRINT LITHOGRAPHY

AMENDMENT PURSUANT TO PCT ARTICLE 34

MAIL STOP PCT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 2213-1450

Sir:

It is respectfully requested that the following Amendments be entered
pursuant to PCT Article 34.

AMENDMENTS

Please amend the application as follows:

IN THE SPECIFICATION:

Please replace pages 11, 15, 16, 18, 22, 24, 32, 33, 38-39, 41, 44-47, and 84
of the specification and replace therewith the new, amended pages 11, 15, 16, 18,
22, 24, 32, 33, 38-39, 41, 44-47, and 84 attached hereto.

IN THE CLAIMS:

Applicant has made the following amendments to the claims in the above-referenced PCT International Application:

Claims 1-6, unchanged;

Claim 7, amended;

Claims 8-59, unchanged;

Claim 60, amended;

Claims 61-80, unchanged;

Claim 81, amended;

Claims 82-102, unchanged;

Claim 103, amended.

IN THE DRAWINGS:

Please substitute page 8/31 for Figures 3E and 3F with the enclosed amended page 8/31 for Figures 3E and 3F.

REMARKS

SPECIFICATION - Pages 11, 15-16, 18, 22, 24, 32-33, 38-39, 41, 44-47, and 84 have been replaced by amended pages 11, 15-16, 18, 22, 24, 32-33, 38-39, 41, 44-47, and 84 to rectify readily apparent typographical and grammatical errors. On page 45, line 24, the term "surface" was inserted after the term "template". Support for this amendment is found on page 45, line 10. On page 47, line 20, the term "surface" was inserted after the term "template". Support for this amendment is found on page 47, lines 6-7.

CLAIMS - The claims have been amended as indicated in amended substitute pages 106, 113, 115-116, and 118 to rectify readily apparent typographical and grammatical errors. Claim 60 was amended by changing the dependency from Claim 59 to Claim 57 to provide proper antecedent for the term "particle".

DRAWINGS - The replacement drawing sheet for Figures 3E and 3F corrects minor typographical errors to the reference numerals for Figure 3E named on the sheet. The reference numerals "308" on the original drawing sheet of Figures 3E has been amended by the replacement sheet to "310". The changes are being made to maintain consistency of reference numerals throughout the application. Support for the correction of "308" to "310" can be found at page 34, lines 1 through 3.

Substitute sheets, pages 11, 15- 16, 18, 22, 24, 32-33, 38-39, 41, 44-47, 84, 106, 113, 115-116, 118, and 8/31 for previous pages 11, 15-16, 18, 22, 24, 32-33, 38-39, 41, 44-47, 84, 106, 113, 115-116, 118, and 8/31 are attached to this cover letter in accordance with Rule 66.8.

The amendments to the specification, claims, and drawings do not add any new matter to the application.

proceeds when taken in connection with the accompanying Drawings and Examples as best described herein below.

BRIEF DESCRIPTION OF THE DRAWINGS

5 Figures 1A-1D are a schematic representation of an embodiment of the presently disclosed method for preparing a patterned template.

 Figures 2A-2F are a schematic representation of the presently disclosed method for forming one or more micro- and/or nanoscale particles.

10 Figures 3A-3F are a schematic representation of the presently disclosed method for preparing one or more spherical particles.

 Figures 4A-4D are a schematic representation of the presently disclosed method for fabricating charged polymeric particles. Fig. 4A represents the electrostatic charging of the molded particle during polymerization or crystallization; Fig. 4B represents a charged nano-disc; Fig. 4C represents typical random juxtapositioning of uncharged nano-discs; and
15 Fig. 4D represents the spontaneous aggregation of charged nano-discs into chain-like structures.

 Figures 5A-5C are a schematic illustration of multilayer particles that can be formed using the presently disclosed soft lithography method.

20 Figures 6A-6C are a schematic representation of the presently disclosed method for making three-dimensional nanostructures using a soft lithography technique.

 Figures 7A-7F are a schematic representation of an embodiment of the presently disclosed method for preparing a multi-dimensional complex
25 structure.

 Figures 8A-8E are a schematic representation of the presently disclosed imprint lithography process resulting in a "scum layer."

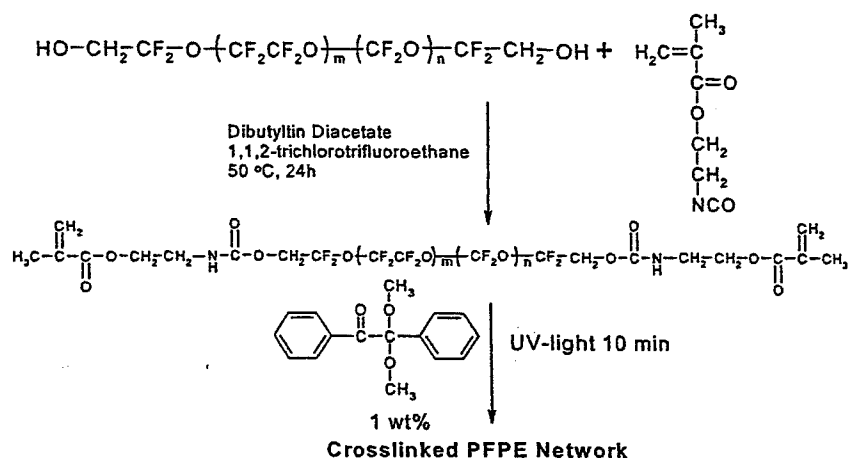
 Figures 9A-9E are a schematic representation of the presently disclosed imprint lithography method, which eliminates the "scum layer" by
30 using a functionalized, non-wetting patterned template and a non-wetting substrate.

comprises a solvent resistant, elastomer-based material, such as but not limited to a fluorinated elastomer-based material.

Further, the presently disclosed subject matter describes the first nano-contact molding of organic materials to generate high fidelity features using an elastomeric mold. Accordingly, the presently disclosed subject matter describes a method for producing free-standing, isolated micro- and nanostructures of any shape using soft or imprint lithography techniques. Representative micro- and nanostructures include but are not limited to micro- and nanoparticles, and micro- and nano-patterned substrates.

The nanostructures described by the presently disclosed subject matter can be used in several applications, including, but not limited to, semiconductor manufacturing, such as molding etch barriers without scum layers for the fabrication of semiconductor devices; crystals; materials for displays; photovoltaics; a solar cell device; optoelectronic devices; routers; gratings; radio frequency identification (RFID) devices; catalysts; fillers and additives; detoxifying agents; etch barriers; atomic force microscope (AFM) tips; parts for nano-machines; the delivery of a therapeutic agent, such as a drug or genetic material; cosmetics; chemical mechanical planarization (CMP) particles; and porous particles and shapes of any kind that will enable the nanotechnology industry.

Representative solvent resistant elastomer-based materials include but are not limited to fluorinated elastomer-based materials. As used herein, the term "solvent resistant" refers to a material, such as an elastomeric material that neither swells nor dissolves in common hydrocarbon-based organic solvents or acidic or basic aqueous solutions. Representative fluorinated elastomer-based materials include but are not limited to perfluoropolyether (PFPE)-based materials. A photocurable liquid PFPE exhibits desirable properties for soft lithography. A representative scheme for the synthesis and photocuring of functional PFPEs is provided in Scheme 1.



Scheme 1. Synthesis and Photocuring of Functional Perfluoropolyethers.

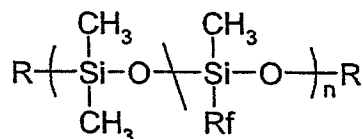
Additional schemes for the synthesis of functional perfluoropolyethers are provided in Examples 7.1 through 7.6.

This PFPE material has a low surface energy (for example, about 12 mN/m); is non-toxic, UV transparent, and highly gas permeable; and cures into a tough, durable, highly fluorinated elastomer with excellent release properties and resistance to swelling. The properties of these materials can be tuned over a wide range through the judicious choice of additives, fillers, reactive co-monomers, and functionalization agents. Such properties that are desirable to modify, include, but are not limited to, modulus, tear strength, surface energy, permeability, functionality, mode of cure, solubility and swelling characteristics, and the like. The non-swelling nature and easy release properties of the presently disclosed PFPE materials allows for nanostructures to be fabricated from any material. Further, the presently disclosed subject matter can be expanded to large scale rollers or conveyor belt technology or rapid stamping that allow for the fabrication of nanostructures on an industrial scale.

In some embodiments, the patterned template comprises a solvent resistant, low surface energy polymeric material derived from casting low viscosity liquid materials onto a master template and then curing the low

In some embodiments, the fluoroolefin material is made from monomers which comprise tetrafluoroethylene, vinylidene fluoride, hexafluoropropylene, 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole, a functional fluoroolefin, functional acrylic monomer, and a functional methacrylic monomer.

In some embodiments, the silicone material comprises a fluoroalkyl functionalized polydimethylsiloxane (PDMS) having the following structure:

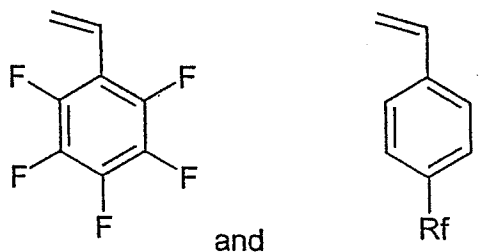


wherein:

R is selected from the group consisting of an acrylate, a methacrylate, and a vinyl group; and

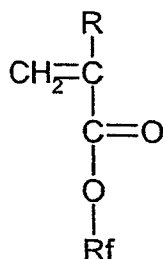
Rf comprises a fluoroalkyl chain.

In some embodiments, the styrenic material comprises a fluorinated styrene monomer selected from the group consisting of:



wherein Rf comprises a fluoroalkyl chain.

In some embodiments, the acrylate material comprises a fluorinated acrylate or a fluorinated methacrylate having the following structure:



wherein:

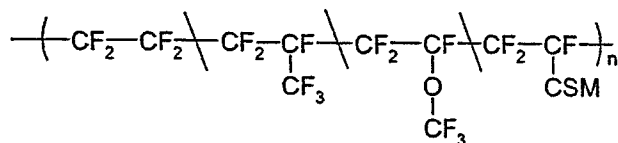
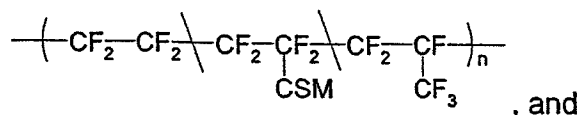
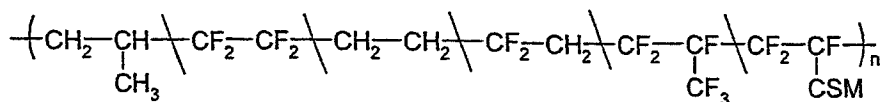
R is selected from the group consisting of H, alkyl, substituted alkyl, aryl, and substituted aryl; and

are produced in a continuous process is schematically presented. An apparatus 199 is provided for carrying out the process. Indeed, while Figure 2F schematically presents a continuous process for particles, apparatus 199 can be adapted for batch processes, and for providing a pattern on a substrate continuously or in batch, in accordance with the presently disclosed subject matter and based on a review of the presently disclosed subject matter by one of ordinary skill in the art.

Continuing, then, with Figure 2F, droplet 204 of liquid material is applied to substrate 200' via reservoir 203. Substrate 200' can be coated or not coated with a non-wetting agent. Substrate 200' and pattern template 108' are placed in a spaced relationship with respect to each other and are also operably disposed with respect to each other to provide for the conveyance of droplet 204 between patterned template 108' and substrate 200'. Conveyance is facilitated through the provision of pulleys 208, which are in operative communication with controller 201. By way of representative non-limiting examples, controller 201 can comprise a computing system, appropriate software, a power source, a radiation source, and/or other suitable devices for controlling the functions of apparatus 199. Thus, controller 201 provides for power for and other control of the operation of pulleys 208 to provide for the conveyance of droplet 204 between patterned template 108' and substrate 200'. Particles 206 are formed and treated between substrate 200' and patterned template 108' by a treating process T_R , which is also controlled by controller 201. Particles 206 are collected in an inspecting device 210, which is also controlled by controller 201. Inspecting device 210 provides for one of inspecting, measuring, and both inspecting and measuring one or more characteristics of particles 206. Representative examples of inspecting devices 210 are disclosed elsewhere herein.

Thus, in some embodiments, the method for forming one or more particles comprises:

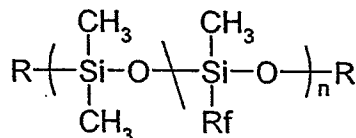
- (a) providing a patterned template and a substrate, wherein the patterned template comprises a first patterned template surface having a plurality of recessed areas formed therein;
- (b) disposing a volume of liquid material in or on at least one of:



wherein CSM comprises a cure site monomer.

5 In some embodiments, the fluoroolefin material is made from monomers which comprise tetrafluoroethylene, vinylidene fluoride, hexafluoropropylene, 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole, a functional fluoroolefin, functional acrylic monomer, and a functional methacrylic monomer.

10 In some embodiments, the silicone material comprises a fluoroalkyl functionalized polydimethylsiloxane (PDMS) having the following structure:

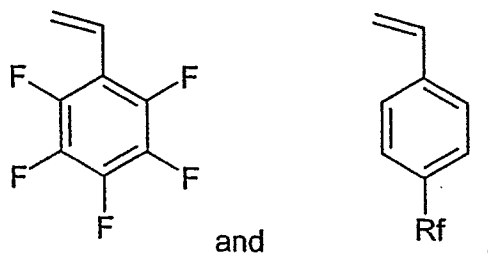


wherein:

15 R is selected from the group consisting of an acrylate, a methacrylate, and a vinyl group; and

Rf comprises a fluoroalkyl chain.

In some embodiments, the styrenic material comprises a fluorinated styrene monomer selected from the group consisting of:



20 wherein Rf comprises a fluoroalkyl chain.

embodiments, the method comprises designing the particles to include a specific biological recognition motif. In some embodiments, the biological recognition motif comprises biotin/avidin and/or other proteins.

5 In some embodiments, the method comprises tailoring the chemical composition of these materials and controlling the reaction conditions, whereby it is then possible to organize the biorecognition motifs so that the efficacy of the particle is optimized. In some embodiments, the particles are designed and synthesized so that recognition elements are located on the surface of the particle in such a way to be accessible to cellular binding sites,
10 wherein the core of the particle is preserved to contain bioactive agents, such as therapeutic molecules. In some embodiments, a non-wetting imprint lithography method is used to fabricate the objects, wherein the objects are optimized for a particular application by incorporating functional motifs, such as biorecognition agents, into the object composition. In some embodiments,
15 the method further comprises controlling the microscale and nanoscale structure of the object by using methods selected from the group consisting of self-assembly, stepwise fabrication procedures, reaction conditions, chemical composition, crosslinking, branching, hydrogen bonding, ionic interactions, covalent interactions, and the like. In some embodiments, the method further
20 comprises controlling the microscale and nanoscale structure of the object by incorporating chemically organized precursors into the object. In some embodiments, the chemically organized precursors are selected from the group consisting of block copolymers and core-shell structures.

25 In sum, the presently disclosed subject matter describes a non-wetting imprint lithography technique that is scalable and offers a simple, direct route to such particles without the use of self-assembled, difficult to fabricate block copolymers and other systems.

30 III. Formation of Rounded Particles Through "Liquid Reduction"

Referring now to Figures 3A through 3F, the presently disclosed subject matter provides a "liquid reduction" process for forming particles that have shapes that are not conformal to the shape of the template, including but not limited to spherical micro- and nanoparticles. For example, a "cube-

shaped" template can allow for spherical particles to be made, whereas a "Block arrow-shaped" template can allow for "loli-pop" shaped particles or objects to be made wherein the introduction of a gas allows surface tension forces to reshape the resident liquid prior to treating it. While not wishing to
5 be bound by any particular theory, the non-wetting characteristics that can be provided in some embodiments of the presently disclosed patterned template and/or treated or coated substrate allows for the generation of rounded, e.g., spherical, particles.

Referring now to Figure 3A, droplet 302 of a liquid material is disposed
10 on substrate 300, which in some embodiments is coated or treated with a non-wetting material 304. A patterned template 108, which comprises a plurality of recessed areas 110 and patterned surface areas 112, also is provided.

Referring now to Figure 3B, patterned template 108 is contacted with
15 droplet 302. The liquid material comprising droplet 302 then enters recessed areas 110 of patterned template 108. In some embodiments, a residual, or "scum," layer RL of the liquid material comprising droplet 302 remains between the patterned template 108 and substrate 300.

Referring now to Figure 3C, a first force F_{a1} is applied to patterned
20 template 108. A contact point CP is formed between the patterned template 108 and the substrate and displacing residual layer RL. Particles 306 are formed in the recessed areas 110 of patterned template 108.

Referring now to Figure 3D, a second force F_{a2} , wherein the force
25 applied by F_{a2} is greater than the force applied by F_{a1} , is then applied to patterned template 108, thereby forming smaller liquid particles 308 inside recessed areas 112 and forcing a portion of the liquid material comprising droplet 302 out of recessed areas 112.

Referring now to Figure 3E, the second force F_{a2} is released, thereby
30 returning the contact pressure to the original contact pressure applied by first force F_{a1} . In some embodiments, patterned template 108 comprises a gas permeable material, which allows a portion of space with recessed areas 112 to be filled with a gas, such as nitrogen, thereby forming a plurality of liquid

7A-7F can be carried out multiple times as desired to form intricate nanostructures.

Accordingly, in some embodiments, a method for forming multidimensional structures is provided, the method comprising:

- 5 (a) providing a particle prepared by the process described in the figures;
- (b) providing a second patterned template;
- (c) disposing a second liquid material in the second patterned template;
- 10 (d) contacting the second patterned template with the particle of step (a); and
- (e) treating the second liquid material to form a multidimensional structure.

15 VII. Imprint Lithography

Referring now to Figures 8A-8D, a method for forming a pattern on a substrate is illustrated. In the embodiment illustrated in Figure 8, an imprint lithography technique is used to form a pattern on a substrate.

Referring now to Figure 8A, a patterned template **810** is provided. In some embodiments, patterned template **810** comprises a solvent resistant, low surface energy polymeric material, derived from casting low viscosity liquid materials onto a master template and then curing the low viscosity liquid materials to generate a patterned template as defined hereinabove. Patterned template **810** further comprises a first patterned template surface **812** and a second template surface **814**. The first patterned template surface **812** further comprises a plurality of recesses **816**. The patterned template derived from a solvent resistant, low surface energy polymeric material could be mounted on another material to facilitate alignment of the patterned template or to facilitate continuous processing such as a conveyor belt. This might be particularly useful in the fabrication of precisely placed structures on a surface, such as in the fabrication of a complex devices or a semiconductor, electronic or photonic devices.

Referring again to Figure 8A, a substrate 820 is provided. Substrate 820 comprises a substrate surface 822. In some embodiments, substrate 820 is selected from the group consisting of a polymer material, an inorganic material, a silicon material, a quartz material, a glass material, and surface treated variants thereof. In some embodiments, at least one of patterned template 810 and substrate 820 has a surface energy lower than 18 mN/m. In some embodiments, at least one of patterned template 810 and substrate 820 has a surface energy lower than 15 mN/m.

In some embodiments, as illustrated in Figure 8A, patterned template 810 and substrate 820 are positioned in a spaced relationship to each other such that first patterned template surface 812 faces substrate surface 822 and a gap 830 is created between first patterned template surface 812 and substrate surface 822. This is an example of a predetermined relationship.

Referring now to Figure 8B, a volume of liquid material 840 is disposed in the gap 830 between first patterned template surface 812 and substrate surface 822. In some embodiments, the volume of liquid material 840 is disposed directed on a non-wetting agent (not shown), which is disposed on first patterned template surface 812.

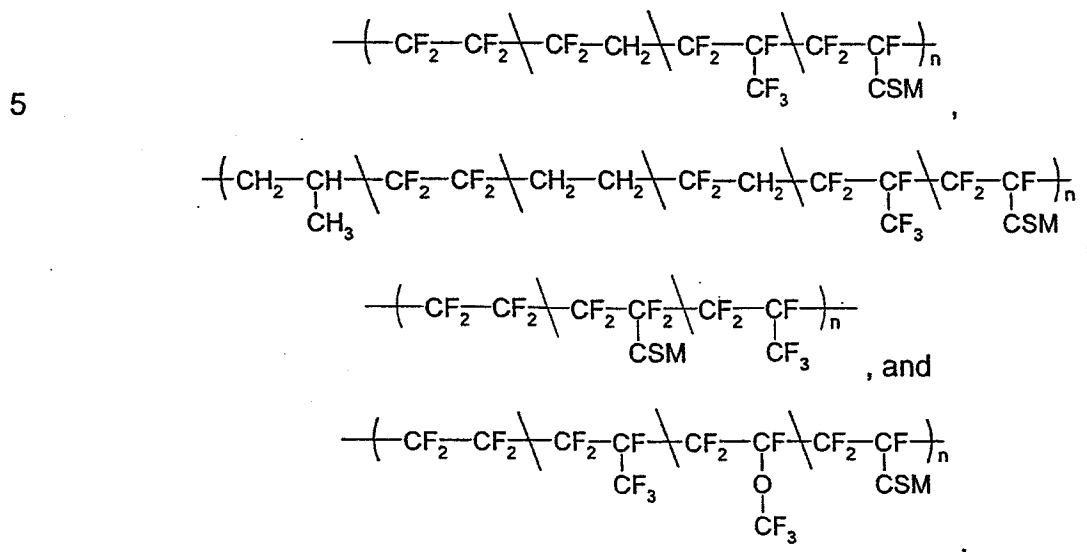
Referring now to Figure 8C, in some embodiments, first patterned template 812 is contacted with the volume of liquid material 840. A force F_a is applied to second template surface 814 thereby forcing the volume of liquid material 840 into the plurality of recesses 816. In some embodiments, as illustrated in Figure 8C, a portion of the volume of liquid material 840 remains between first patterned template surface 812 and substrate surface 820 after force F_a is applied.

Referring again to Figure 8C, in some embodiments, the volume of liquid material 840 is treated by a treating process T_r while force F_a is being applied to form a treated liquid material 842. In some embodiments, treating process T_r comprises a process selected from the group consisting of a thermal process, a photochemical process, and a chemical process.

Referring now to Figure 8D, a force F_r is applied to patterned template 810 to remove patterned template 810 from treated liquid material 842 to reveal a pattern 850 on substrate 820 as shown in Figure 8E. In some

wherein X is present or absent, and when present comprises an endcapping group.

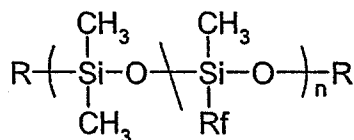
In some embodiments, the fluoroolefin material is selected from the group consisting of:



wherein CSM comprises a cure site monomer.

10 In some embodiments, the fluoroolefin material is made from monomers which comprise tetrafluoroethylene, vinylidene fluoride, hexafluoropropylene, 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole, a functional fluoroolefin, functional acrylic monomer, and a functional methacrylic monomer.

15 In some embodiments, the silicone material comprises a fluoroalkyl functionalized polydimethylsiloxane (PDMS) having the following structure:



wherein:

20 R is selected from the group consisting of an acrylate, a methacrylate, and a vinyl group; and

Rf comprises a fluoroalkyl chain.

In some embodiments, the styrenic material comprises a fluorinated styrene monomer selected from the group consisting of:

In some embodiments, the disposing of the volume of liquid material is regulated by a spreading process. In some embodiments, the spreading process comprises:

- 5 (a) disposing a first volume of liquid material on the patterned template to form a layer of liquid material on the patterned template; and
- (b) drawing an implement across the layer of liquid material to:
 - (i) remove a second volume of liquid material from the layer of liquid material on the patterned template; and
 - 10 (ii) leave a third volume of liquid material on the patterned template.

In some embodiments, the contacting of the first template surface with the substrate eliminates essentially all of the disposed volume of liquid material.

15 In some embodiments, the treating of the liquid material comprises a process selected from the group consisting of a thermal process, a photochemical process, and a chemical process.

In some embodiments, the method comprises a batch process. In some embodiments, the batch process is selected from one of a semi-batch process and a continuous batch process.

20 In some embodiments, the presently disclosed subject matter describes a patterned substrate formed by the presently disclosed methods.

VIII. Imprint Lithography Free of a Residual "Scum Layer"

25 A characteristic of imprint lithography that has restrained its full potential is the formation of a "scum layer" once the liquid material, e.g., a resin, is patterned. The "scum layer" comprises residual liquid material that remains between the stamp and the substrate. In some embodiments, the presently disclosed subject matter provides a process for generating patterns essentially free of a scum layer.

30 Referring now to Figures 9A-9E, in some embodiments, a method for forming a pattern on a substrate is provided, wherein the pattern is essentially free of a scum layer. Referring now to Figure 9A, a patterned template 910 is provided. Patterned template 910 further comprises a first patterned template

surface 912 and a second template surface 914. The first patterned template surface 912 further comprises a plurality of recesses 916. In some embodiments, a non-wetting agent 960 is disposed on the first patterned template surface 912.

5 Referring again to Figure 9A, a substrate 920 is provided. Substrate 920 comprises a substrate surface 922. In some embodiments, a non-wetting agent 960 is disposed on substrate surface 920.

10 In some embodiments, as illustrated in Figure 9A, patterned template 910 and substrate 920 are positioned in a spaced relationship to each other such that first patterned template surface 912 faces substrate surface 922 and a gap 930 is created between first patterned template surface 912 and substrate surface 922.

15 Referring now to Figure 9B, a volume of liquid material 940 is disposed in the gap 930 between first patterned template surface 912 and substrate surface 922. In some embodiments, the volume of liquid material 940 is disposed directly on first patterned template surface 912. In some embodiments, the volume of liquid material 940 is disposed directly on non-wetting agent 960, which is disposed on first patterned template surface 912. In some embodiments, the volume of liquid material 940 is disposed directly on substrate surface 920. In some embodiments, the volume of liquid material 940 is disposed directly on non-wetting agent 960, which is disposed on substrate surface 920.

20 Referring now to Figure 9C, in some embodiments, first patterned template surface 912 is contacted with the volume of liquid material 940. A force F_a is applied to second template surface 914 thereby forcing the volume of liquid material 940 into the plurality of recesses 916. In contrast with the embodiment illustrated in Figure 8, a portion of the volume of liquid material 940 is forced out of gap 930 by force F_o when force F_a is applied.

25 Referring again to Figure 9C, in some embodiments, the volume of liquid material 940 is treated by a treating process T_r while force F_a is being applied to form a treated liquid material 942.

Referring now to Figure 9D, a force F_r is applied to patterned template 910 to remove patterned template 910 from treated liquid material 942 to reveal a pattern 950 on substrate 920 as shown in Figure 9E. In this embodiment, substrate 920 is essentially free of a residual, or "scum," layer of treated liquid material 942.

In some embodiments, at least one of the template surface and substrate comprises a functionalized surface element. In some embodiments, the functionalized surface element is functionalized with a non-wetting material. In some embodiments, the non-wetting material comprises functional groups that bind to the liquid material. In some embodiments, the non-wetting material is selected from the group consisting of a trichloro silane, a trialkoxy silane, a trichloro silane comprising non-wetting and reactive functional groups, a trialkoxy silane comprising non-wetting and reactive functional groups, and mixtures thereof.

In some embodiments, the point of contact between the two surface elements is free of liquid material. In some embodiments, the point of contact between the two surface elements comprises residual liquid material. In some embodiments, the height of the residual liquid material is less than 30% of the height of the structure. In some embodiments, the height of the residual liquid material is less than 20% of the height of the structure. In some embodiments, the height of the residual liquid material is less than 10% of the height of the structure. In some embodiments, the height of the residual liquid material is less than 5% of the height of the structure. In some embodiments, the volume of liquid material is less than the volume of the patterned template. In some embodiments, substantially all of the volume of liquid material is confined to the patterned template of at least one of the surface elements. In some embodiments, having the point of contact between the two surface elements free of liquid material retards slippage between the two surface elements.

IX. Solvent-Assisted Micro-molding (SAMIM)

In some embodiments, the presently disclosed subject matter describes a solvent-assisted micro-molding (SAMIM) method for forming a pattern on a substrate.

5 Referring now to Figure 10A, a patterned template **1010** is provided. Patterned template **1010** further comprises a first patterned template surface **1012** and a second template surface **1014**. The first patterned template surface **1012** further comprises a plurality of recesses **1016**.

10 Referring again to Figure 10A, a substrate **1020** is provided. Substrate **1020** comprises a substrate surface **1022**. In some embodiments, a polymeric material **1070** is disposed on substrate surface **1022**. In some embodiments, polymeric material **1070** comprises a resist polymer.

15 Referring again to Figure 10A, patterned template **1010** and substrate **1020** are positioned in a spaced relationship to each other such that first patterned template surface **1012** faces substrate surface **1022** and a gap **1030** is created between first patterned template surface **1012** and substrate surface **1022**. As shown in Figure 10A, a solvent **S** is disposed within gap **1030**, such that solvent **S** contacts polymeric material **1070** forming a swollen polymeric material **1072**.

20 Referring now to Figures 10B and 10C, first patterned template surface **1012** is contacted with swollen polymeric material **1072**. A force F_a is applied to second template surface **1014** thereby forcing a portion of swollen polymeric material **1072** into the plurality of recesses **1016** and leaving a portion of swollen polymeric material **1072** between first patterned template surface **1012** and substrate surface **1020**. The swollen polymeric material **1072** is then treated by a treating process T_r while under pressure.

25 Referring now to Figure 10D, a force F_r is applied to patterned template **1010** to remove patterned template **1010** from treated swollen polymeric material **1072** to reveal a polymeric pattern **1074** on substrate **1020** as shown in Figure 10E.

30

established. By repeating this methodology with different particle formulations, many combinations of therapeutic agents, tissue targeting agents, release agents, and other important compounds can be rapidly screened to determine the optimal combination for a desired therapeutic application.

Example 3.26 Fabrication of a shape-specific PEG membrane

A patterned perfluoropolyether (PFPE) mold is generated by pouring a PFPE-dimethacrylate (PFPE-DMA) containing 1-hydroxycyclohexyl phenyl ketone over a silicon substrate patterned with 3- μm cylindrical holes that are 5 μm deep. A poly(dimethylsiloxane) mold is used to confine the liquid PFPE-DMA to the desired area. The apparatus is then subjected to UV light ($\lambda = 365 \text{ nm}$) for 10 minutes while under a nitrogen purge. The fully cured PFPE-DMA mold is then released from the silicon master. Separately, a poly(ethylene glycol) (PEG) diacrylate ($n=9$) is blended with 1 wt% of a photoinitiator, 1-hydroxycyclohexyl phenyl ketone. Flat, uniform, non-wetting surfaces are generated by treating a silicon wafer cleaned with "piranha" solution (1:1 concentrated sulfuric acid:30% hydrogen peroxide (aq) solution) with trichloro(1H, 1H, 2H, 2H-perfluorooctyl) silane via vapor deposition in a desiccator for 20 minutes. Following this, 50 μL of PEG diacrylate is then placed on the treated silicon wafer and the patterned PFPE mold placed on top of it. The substrate is then placed in a molding apparatus and a small pressure is applied to push out excess PEG-diacrylate. The entire apparatus is then subjected to UV light ($\lambda = 365 \text{ nm}$) for ten minutes while under a nitrogen purge. An interconnected membrane is observed after separation of the PFPE mold and the treated silicon wafer using scanning electron microscopy (SEM). The membrane is released from the surface by soaking in water and allowing it to lift off the surface.

DEPOSIT ACCOUNT

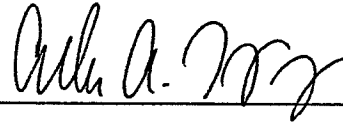
Although it is believed that no fee is due in this matter, the Commissioner is hereby authorized to charge any deficiencies or credit any overpayment in connection with the filing of this correspondence to Deposit Account No. 50-0426.

Respectfully submitted,

JENKINS, WILSON & TAYLOR, P.A.

Date: 26 May 2005

By: _____



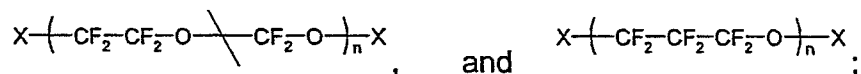
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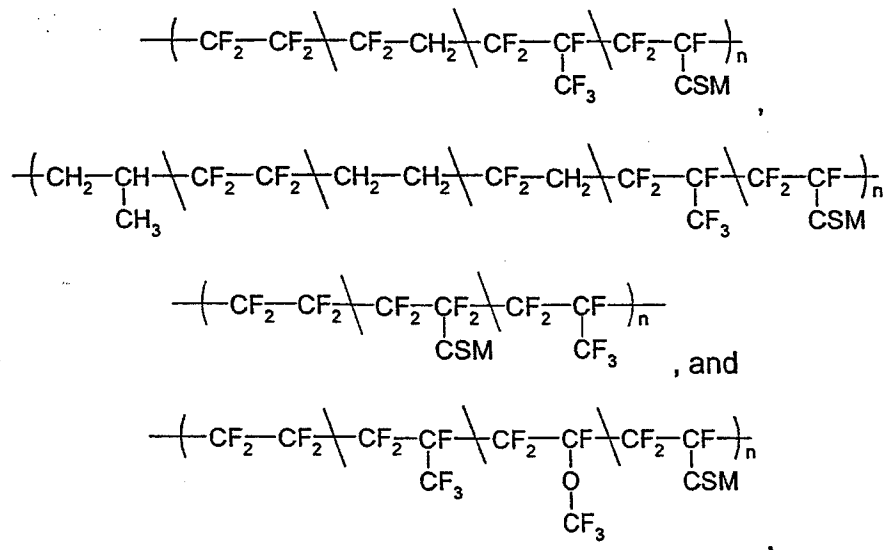
Enclosures:

Replacement pages 11, 15, 16, 18, 22, 24, 32, 33, 38-39, 41, 44-47, 84, 106, 113, 115-116, 118, and 8/31



wherein X is present or absent, and when present comprises an endcapping group.

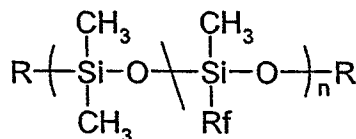
6. The method of Claim 4, wherein the fluoroolefin material is selected from the group consisting of:



- wherein CSM comprises a cure site monomer.

7. The method of Claim 4, wherein the fluoroolefin material is made from monomers which comprise tetrafluoroethylene, vinylidene fluoride, hexafluoropropylene, 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole, a functional fluoroolefin, functional acrylic monomer, and a functional methacrylic monomer.

8. The method of Claim 4, wherein the silicone material comprises a fluoroalkyl functionalized polydimethylsiloxane (PDMS) having the following structure:



- wherein:

R is selected from the group consisting of an acrylate, a methacrylate, and a vinyl group; and

Rf comprises a fluoroalkyl chain.

- (c) delivering the particle comprising the therapeutic agent to the target.

58. The method of Claim 57, wherein the therapeutic agent is selected from one of a drug and genetic material.

5 59. The method of Claim 58, wherein the genetic material is selected from the group consisting of a non-viral gene vector, DNA, RNA, RNAi, and a viral particle.

60. The method of Claim 57, wherein the particle comprises a biodegradable polymer.

10 61. The method of Claim 60, wherein the biodegradable polymer is selected from the group consisting of a polyester, a polyanhydride, a polyamide, a phosphorous-based polymer, a poly(cyanoacrylate), a polyurethane, a polyorthoester, a polydihydropyran, and a polyacetal.

15 62. The method of Claim 61, wherein the polyester is selected from the group consisting of polylactic acid, polyglycolic acid, poly(hydroxybutyrate), poly(ϵ -caprolactone), poly(β -malic acid), and poly(dioxanones).

20 63. The method of Claim 61, wherein the polyanhydride is selected from the group consisting of poly(sebacic acid), poly(adipic acid), and poly(terphthalic acid).

64. The method of Claim 61, wherein the polyamide is selected from the group consisting of poly(imino carbonates) and polyaminoacids.

25 65. The method of Claim 61, wherein the phosphorous-based polymer is selected from the group consisting of a polyphosphate, a polyphosphonate, and a polyphosphazene.

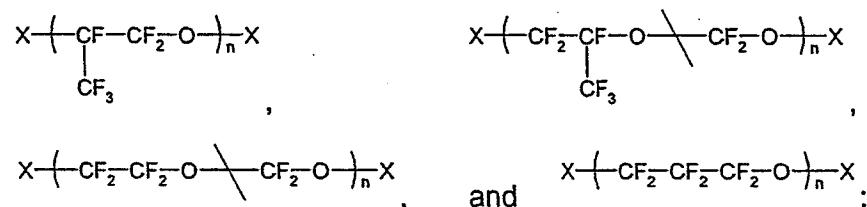
66. The method of Claim 60, wherein the biodegradable polymer further comprises a polymer that is responsive to a stimulus.

30 67. The method of Claim 66, wherein the stimulus is selected from the group consisting of pH, radiation, ionic strength, temperature, an alternating magnetic field, and an alternating electric field.

68. The method of Claim 67, wherein the stimulus comprises an alternating magnetic field.

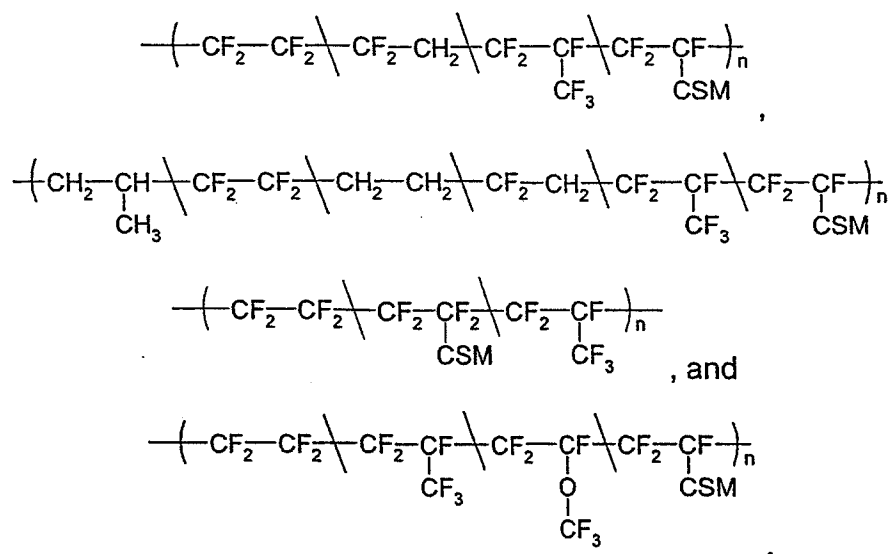
78. The method of Claim 76, wherein at least one of the patterned template and substrate comprises a material selected from the group consisting of a perfluoropolyether material, a fluoroolefin material, an acrylate material, a silicone material, a styrenic material, a fluorinated thermoplastic elastomer (TPE), a triazine fluoropolymer, a perfluorocyclobutyl material, a fluorinated epoxy resin, and a fluorinated monomer or fluorinated oligomer that can be polymerized or crosslinked by a metathesis polymerization reaction.

79. The method of Claim 78, wherein the perfluoropolyether material comprises a backbone structure selected from the group consisting of:



wherein X is present or absent, and when present comprises an endcapping group.

80. The method of Claim 78, wherein the fluoroolefin material is selected from the group consisting of:

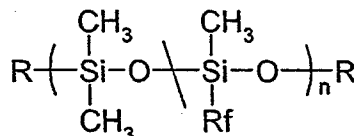


wherein CSM comprises a cure site monomer.

81. The method of Claim 78 wherein the fluoroolefin material is made from monomers which comprise tetrafluoroethylene, vinylidene fluoride,

hexafluoropropylene, 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole, a functional fluoroolefin, functional acrylic monomer, and a functional methacrylic monomer.

82. The method of Claim 78, wherein the silicone material comprises a fluoroalkyl functionalized polydimethylsiloxane (PDMS) having the following structure:

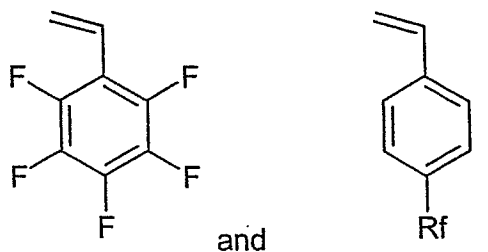


wherein:

R is selected from the group consisting of an acrylate, a methacrylate, and a vinyl group; and

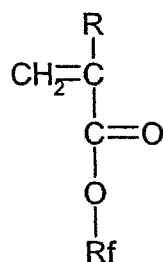
Rf comprises a fluoroalkyl chain.

83. The method of Claim 78, wherein the styrenic material comprises a fluorinated styrene monomer selected from the group consisting of:



wherein Rf comprises a fluoroalkyl chain.

84. The method of Claim 78, wherein the acrylate material comprises a fluorinated acrylate or a fluorinated methacrylate having the following structure:



wherein:

97. The method of Claim 94, wherein the plurality of structural features has a dimension ranging from about 1 micron to about 100 nm in size.

5 98. The method of Claim 94, wherein the plurality of structural features has a dimension ranging from about 100 nm to about 1 nm in size.

99. The method of Claim 76, wherein the liquid material is selected from the group consisting of a polymer, a solution, a monomer, a plurality of monomers, a polymerization initiator, a polymerization catalyst, an inorganic precursor, a metal precursor, a pharmaceutical agent, a tag, a magnetic material, a paramagnetic material, a superparamagnetic material, a ligand, a cell penetrating peptide, a porogen, a surfactant, a plurality of immiscible liquids, a solvent, and a charged species.

100. The method of Claim 99, wherein the pharmaceutical agent is selected from the group consisting of a drug, a peptide, RNAi, and DNA.

15 101. The method of Claim 99, wherein the tag is selected from the group consisting of a fluorescence tag, a radiolabeled tag, and a contrast agent.

102. The method of Claim 99, wherein the ligand comprises a cell targeting peptide.

20 103. The method of Claim 76, wherein the liquid material is selected from one of a resist polymer and a low-k dielectric.

104. The method of Claim 76, wherein the liquid material comprises a non-wetting agent.

25 105. The method of Claim 76, wherein the disposing of the volume of liquid material is regulated by a spreading process.

106. The method of Claim 105, wherein the spreading process comprises:

- 30
- (a) disposing a first volume of liquid material on the patterned template to form a layer of liquid material on the patterned template; and
 - (b) drawing an implement across the layer of liquid material to:
 - (i) remove a second volume of liquid material from the layer of liquid material on the patterned template; and

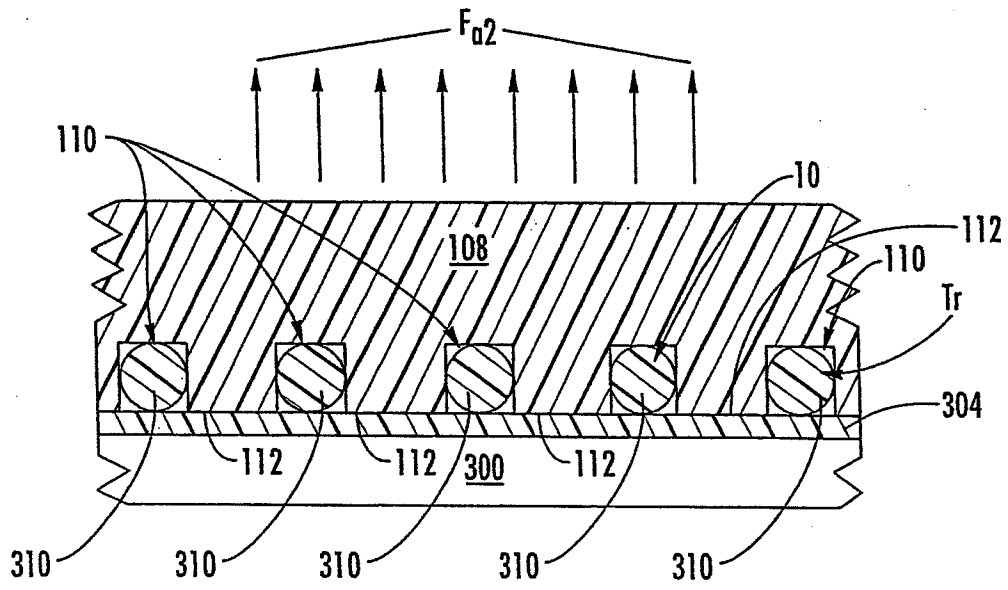


FIG. 3E

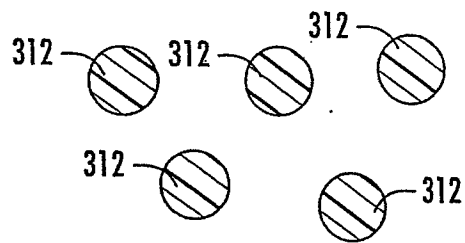


FIG. 3F